



# Photocatalytic degradation of organic pollutants on surface anionized $\text{TiO}_2$ : Common effect of anions for high hole-availability by water



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## ABSTRACT

Effects of  $\text{TiO}_2$  surface anionization by inorganic anions such as phosphate, fluoride and sulfate on the photocatalytic degradation behaviors of a series of model pollutants are systematically investigated. The degradation rate, accumulation of hydrogen peroxide, formation of hydroxyl radicals and zeta potential are compared in the presence of different anions. Our experimental results show that specific-adsorbed anions have similar effect on all the tested photocatalytic parameters in all the systems, although the extent is anion-dependent. These observations indicate that the previously studied effect of surface fluorination is not special, and it is only an example of anionization effects. In combination with DFT calculation, we propose a common mechanism for anionization effect. According to this mechanism, the anion-derived surface negative charges are able to draw the photogenerated holes to  $\text{TiO}_2$  surface by electrostatic force. Thus, more holes are available at the interface, which accelerates remarkably the oxidation of surface-adsorbed solvent water to free  $\cdot\text{OH}$  radicals.

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## 1. Introduction

$\text{TiO}_2$  photocatalysis has attracted persistent attention because of its promising applications in water purification as well as solar energy conversion [1]. During photocatalysis, following the excitation of photocatalyst ( $\text{TiO}_2$ ), the pairs of valence band hole ( $\text{h}_{\text{vb}}^+$ ) and conduction band electron ( $\text{e}_{\text{cb}}^-$ ) are first formed. Subsequently, the  $\text{h}_{\text{vb}}^+$  and  $\text{e}_{\text{cb}}^-$  are transported to the  $\text{TiO}_2$  surface, where they may initiate oxidation and reduction reactions, respectively. On the other hand, the  $\text{h}_{\text{vb}}^+$  and  $\text{e}_{\text{cb}}^-$  undergo massive recombination at the surface or in the bulk of the photocatalyst, which competes with their desirable transfer to the surface adsorbed species and limits the overall efficiency of charge separation. Accordingly, enhancement in the transport of photogenerated carriers toward surface and consequently their availability to adsorbed species is the most used strategy to accelerate the photocatalytic reaction. Practically, such enhancement is usually accomplished by tuning the surface conditions of the semiconductor.

Recently, modification of  $\text{TiO}_2$  surface by  $\text{F}^-$  has attracted remarkable attention [2–4]. It was reported that when  $\text{F}^-$  absorbed specifically on  $\text{TiO}_2$  surface under acidic conditions, the photocatalytic oxidation rate of some organic pollutants such as phenol [2,5,6], benzoic acid [7], acid orange [5] and azo dye Acid Red

[7,8] could be enhanced, while the photooxidation of other pollutants like dichloroacetate [5] and formic acid [7,9] was clearly suppressed. It is important to figure out how and why the presence of  $\text{F}^-$  anions can affect the photocatalytic degradation processes. However, despite of extensive investigation, the understanding on the operative mechanism of fluorination effect is still unsystematic and ambiguous. Diverse interpretations have been proposed, but no consensus is reached so far. For example, when Minero et al. [2] first found the fluorination effect, they suggested that the displacement of surface hydroxyl groups by fluoride suppressed the formation of surface-trapped radicals ( $\equiv\text{TiO}^\bullet$ ) but enhanced the formation of free  $\cdot\text{OH}$  radicals. If the replacement is the only effect, the existence of  $\text{F}^-$  barrier between  $\text{TiO}_2$  and water should make the hole abstraction more difficult, rather than to enhance the oxidation process. Park and Choi [5] proposed another interpretation by ascribing the enhancement effect of  $\text{F}^-$  to the trapping of  $\text{e}_{\text{cb}}^-$ . They assumed that the surface  $\equiv\text{Ti}=\text{F}$  groups were able to serve as effective trapping sites by tightly holding the electrons due to the strong electronegativity of fluorine, and consequently depressed the recombination of electrons and holes. Xu et al. [6] suggested that the enhanced production of free  $\cdot\text{OH}$  radicals was due to the desorption of surface-bound  $\cdot\text{OH}$  radicals by  $\text{F}^-$  in the solution through the formation of  $\cdot\text{OH}\dots\text{F}^-$  hydrogen bond. The work by Macyk and co-workers [10] implied the mechanism that the surface fluorination of  $\text{TiO}_2$  suppressed the interfacial electron transfer and enhanced the energy transfer to generate singlet oxygen.

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The surface modification by other inorganic anions such as  $\text{PO}_4^{3-}$  and  $\text{SO}_4^{2-}$ , although less intensive than the surface fluorination, also arouses extensive interests in the  $\text{TiO}_2$  photocatalysis. However, the reported effects of these anions on the photocatalytic behaviors of  $\text{TiO}_2$  are rather contradictory [11–19], which is mainly due to the different modification processes and the reaction conditions. In our previous work, based on photocatalytic degradation kinetics of various pollutants in the present of phosphate anions, we speculated that the phosphate anion that specifically adsorbed on  $\text{TiO}_2$  surface presented similar effect on the photocatalytic performance to fluoride [11]. If this is true, they should share a common operative mechanism about their effect on photocatalytic processes, and the mechanisms proposed so far are not able to explain well this similarity.

In this study, under the same conditions, we compared systematically the effects of  $\text{F}^-$ ,  $\text{PO}_4^{3-}$  and  $\text{SO}_4^{2-}$  anions on the photocatalytic behaviors by simply adsorbing or preadsorbing these anions on the surface of  $\text{TiO}_2$ . Our experimental results showed that the specifically-adsorbed anion  $\text{PO}_4^{3-}$  had nearly the same effect on all the tested photocatalytic properties in the photooxidation of all these organic pollutants examined as  $\text{F}^-$ ,  $\text{SO}_4^{2-}$  also had the similar effect, although less obvious, as that of  $\text{F}^-$  or  $\text{PO}_4^{3-}$ . It proves definitely that the effect of surface fluorination is not special, and it is only an example of anionization effect. In combination with further DFT calculation, we further propose a common electrostatic-force-based mechanism of surface anionization effects to demonstrate that the specifically adsorbed anions on the  $\text{TiO}_2$  surface are able to greatly enhance the separation of photogenerated carrier, and promote holes to move to the catalyst surface to react with the surface-adsorbed water. This mechanism can interpret well the experimental observations of, for example, the enhanced formation of free  $\cdot\text{OH}$  radicals, and the substrate-dependence of the anion effect, in both the present studies and the earlier reports. Considering that the common inorganic anions (such as  $\text{PO}_4^{3-}$  and  $\text{SO}_4^{2-}$ ) frequently present in natural and industrial wastewater, and their corresponding acids are commonly used to adjust pH or as a pH buffer (for example  $\text{PO}_4^{3-}$ ) in the studies of photocatalysis, the finding on anionization effect should be important to the design of high-efficiency photocatalysts or the practical application of  $\text{TiO}_2$  photocatalysis.

## 2. Experimental

### 2.1. Materials

$\text{TiO}_2$  used in photocatalytic reactions was commercially available Degussa P25, containing 80% anatase and 20% rutile. Deionized water (Millipore, Milli-Q, resistivity 18.2  $\text{M}\Omega\text{ cm}$ ) was used throughout this study.  $\text{NaF}$ ,  $\text{Na}_2\text{SO}_4$  and  $\text{NaH}_2\text{PO}_4$  were purchased from Alfa Aesar. To test the photocatalytic activity of  $\text{TiO}_2$  modified with different anions, organic substrates such as formic acid, phenol, benzene and benzoic acid were also purchased from Alfa Aesar. pH of the solution was adjusted with dilute aqueous solution of  $\text{HClO}_4$  because  $\text{ClO}_4^-$  has low adsorption ability on the surface of metal oxides and is stable during the photocatalytic processes [20].

### 2.2. Photodegradation reaction

The light source used was a 100-W mercury lamp with a filter to remove the irradiation of  $\lambda < 350\text{ nm}$ . 50 mL aqueous solutions (pH 3.5) containing substrates and 1 g/L  $\text{TiO}_2$  powder, with or without the addition of 2 mM anions ( $\text{F}^-$ ,  $\text{PO}_4^{3-}$  or  $\text{SO}_4^{2-}$ ), were placed in a Pyrex vessel. Prior to irradiation, the suspensions were magnetically stirred in the dark for 30 min to ensure the establishment of an

adsorption/desorption equilibrium. At a given time, 3 mL aliquots were collected, centrifuged, and then filtered through a Millipore filter (pore size 0.22  $\mu\text{m}$ ) to remove the solid catalyst particles. The filtrate was then subjected to an analysis of the concentration of the substrates by high-performance liquid chromatography (HPLC, Dionex P580 pump and UVD340S diode array detector) or ion chromatography (IC, Dionex ICS-900). The measurement of intermediate  $\text{H}_2\text{O}_2$  was carried out by a DPD-POD method [21]. The hydroxyl radical generated was trapped by DMPO and then measured by a Bruker model ESP 500E electron paramagnetic resonance (EPR) spectrometer. The samples for EPR measurements were prepared as follow: 5 mL suspension (with or without 2 mM anions, pH 3.5) with 1 g/L  $\text{TiO}_2$  and 40 mM DMPO was exposed to a 100-W mercury lamp under aerated and stirring conditions. 30  $\mu\text{L}$  suspension was collected at time interval of 30 s and filled into a quartz capillary for EPR measurements.

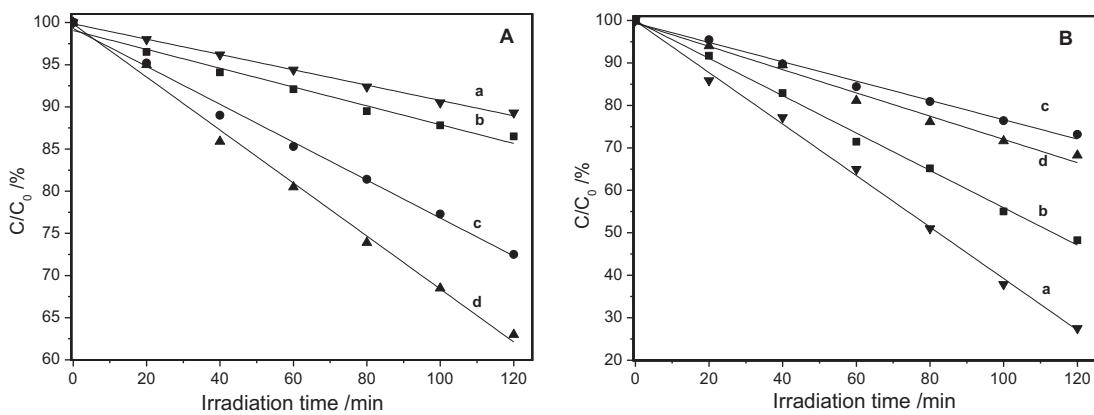
### 2.3. Computational methods

(101) surface anatase  $\text{TiO}_2$ , which is known to be the most exposed crystal facet in P25, was modeled with a periodical slab by DFT method. It had been shown that the two-layer slab was sufficient to model the adsorption of small molecules on anatase (101) surface [22]. To highlight the electron distribution in the surface layer, a four-layer surface slab, containing 96 atoms (32 Ti and 64 O), was employed in this study. The generalized gradient approximation (GGA) [23,24] with a PBE exchange-correlation functional in spin-unrestricted or spin-restricted manner was adopted for geometry optimization. Implicit solvation of water was incorporated into all simulations by use of COSMO-ibs model [25].

Since  $\text{F}^-$  was reported to be able to displace almost all the surface hydroxyl groups on the surface of  $\text{TiO}_2$  at pH 3.5–4.0 [26], during our simulation, all the surface Ti sites was covered by  $\text{F}^-$  anion, and the proton was placed on the 2-coordinated bridged O atom to construct an electrically neutral surface. The adsorption of phosphates on the surface Ti sites had different surface coverage and configurations. Only 1/2 monolayer coverage was considered in this study. In agreement with the experimental study [27], the monodissociative bidentate mode was identified to be the most stable configurations. In this mode, two P=Os of the phosphoric acid were bound up with two adjacent  $\text{Ti}_{5c}$ . One P—OH interacted with the  $\text{O}_{2c}$  by hydrogen bound to form  $\text{OH}-\text{O}_{2c}$ . The dissociated proton was adsorbed on another  $\text{O}_{2c}$ .  $\text{Ti}_{5c}$  and  $\text{O}_{2c}$  were referred to surface titanium and oxygen atoms, respectively. To model the negative charges on the fluorinated or phosphorylated surface, we removed one proton from  $\text{O}_{2c}$ , while, an excess proton was added onto  $\text{O}_{2c}$  to obtain a positive surface in hydrated case. The distribution of conduction band electron and valence band hole in neutral or charged surface, a single excess electron ( $e^-$ ) and a single hole ( $h^+$ ) were added separately in the supercell. All DFT calculations were performed with the DMol<sub>3</sub> packages [28,29] in the Accelrys Materials Studio modeling suite. Other details for the calculations are included in Supplementary Data.

## 3. Results and discussion

As shown in Fig. 1 and Fig. A.1, the presence of  $\text{PO}_4^{3-}$  or  $\text{SO}_4^{2-}$  in  $\text{TiO}_2$  suspensions caused the similar effect on the degradation of different substrates to that of surface fluorination. The general influencing extent of the three anions on the degradation rate was  $\text{F}^- > \text{PO}_4^{3-} > \text{SO}_4^{2-}$  for the same substrate. Compared to naked  $\text{TiO}_2$ , the presence of  $\text{F}^-$ ,  $\text{PO}_4^{3-}$  or  $\text{SO}_4^{2-}$  greatly enhanced the degradation of benzoic acid (BA), benzene and phenol (Fig. 1A, Fig. A.1A and B), but markedly inhibited the degradation of formic acid (FA) (Fig. 1B). For example, as summarized in Table 1, the apparent



**Fig. 1.** Decay of benzoic acid (A) and formic acid (B) with the irradiation time during its photocatalytic degradation in the absence (a) and presence of various anions (b,  $\text{SO}_4^{2-}$ , c,  $\text{PO}_4^{3-}$ , d,  $\text{F}^-$ ). Initial concentration of BA: 0.5 mM; FA: 2 mM;  $\text{TiO}_2$ : 1 g/L; Concentration of anions: 2 mM; pH 3.5.

zero-order rate constants for the degradation of BA are  $1.55 \times 10^{-3}$ ,  $1.1 \times 10^{-3}$  and  $5.5 \times 10^{-4}$  mmol min $^{-1}$  in the presence of  $\text{F}^-$ ,  $\text{PO}_4^{3-}$  or  $\text{SO}_4^{2-}$ , respectively, which was larger than that in the naked  $\text{TiO}_2$  systems ( $4.5 \times 10^{-4}$  mmol min $^{-1}$ ). For FA, the degradation rate was decreased from  $1.22 \times 10^{-2}$  mmol min $^{-1}$  for naked  $\text{TiO}_2$  to  $8.8 \times 10^{-3}$ ,  $4.6 \times 10^{-3}$ , and  $5.4 \times 10^{-3}$  mmol min $^{-1}$  after adding  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ , and  $\text{F}^-$ , respectively.

As shown in Table 1, the change on the adsorption of the substrates on  $\text{TiO}_2$  surface was distinctive with different substrates, for the weakly adsorbed benzene and phenol, almost no influence was exerted by the addition of anions, whereas, for BA and FA, the competitive adsorption of the anions blocked the adsorption of BA and FA. The change in the adsorption on  $\text{TiO}_2$  surface will certainly affect the transfer of  $\text{h}_{\text{vb}}^+$  and  $\text{e}_{\text{cb}}^-$  to substrates and  $\text{O}_2$ , respectively, and consequently influence the photodegradation of the substrates. However, the change in the degradation rate after addition of anions does not completely correlate to the change on the adsorption of substrates on  $\text{TiO}_2$ . For example, the adsorption of BA is greatly inhibited, but the degradation is largely enhanced by the anions. By contrast, the adsorption of FA decreases by competitive adsorption of anions either, but its degradation is markedly depressed instead. It is evident that the alteration on photocatalytic processes in the presence of anions is not merely attributed to the change in the substrate-adsorption caused by anions.

To further understand the effect of the anions, we preadsorbed fluoride, sulfate and phosphate ions on  $\text{TiO}_2$  surface before photocatalytic reactions. After heating 350 °C for 2 h to enhance the bonding of anions with  $\text{TiO}_2$ , the photocatalysts were washed thoroughly with water, and then photocatalytic reactions were carried out in aqueous suspensions of these pretreated photocatalysts without adding extra anions. By such preadsorption, only a small fraction of surface-adsorbed anions can diffuse away from the surface under photocatalytic conditions. Thus, the effect of anions

in the bulk solution can be minimized comparing to that of the surface-bound ones. It was observed that, similar to the situation by directly adding anions into the suspensions, the preadsorbed  $\text{F}^-$ ,  $\text{PO}_4^{3-}$  or  $\text{SO}_4^{2-}$  accelerated and hindered the degradation of BA and FA, respectively (Fig. A.2, inset), which indicates that the effect of anions on the photocatalytic activity of  $\text{TiO}_2$  is definitely attributed to the surface-bound anions, rather than to those in the bulk solution.

Fig. 2 and Fig. A.3 showed the concentration change of  $\text{H}_2\text{O}_2$  during photocatalytic degradation of BA, FA, benzene and phenol on  $\text{TiO}_2$  with or without anions. During the degradation of BA, addition of  $\text{F}^-$ ,  $\text{PO}_4^{3-}$ , or  $\text{SO}_4^{2-}$  suppressed the accumulation of  $\text{H}_2\text{O}_2$ . The depressive effect of  $\text{F}^-$  and  $\text{PO}_4^{3-}$  was more significant than that of  $\text{SO}_4^{2-}$ . By contrast, the anions exhibited opposite effect on the  $\text{H}_2\text{O}_2$  accumulation during the photodegradation of FA, that was, the concentration of  $\text{H}_2\text{O}_2$  in FA system was markedly enhanced by all the anions. The enhancing extent was in an order of  $\text{F}^- > \text{PO}_4^{3-} > \text{SO}_4^{2-}$ . During photocatalytic degradation of benzene, the presence of anions also promoted the accumulation of  $\text{H}_2\text{O}_2$ , although the observed concentration was rather low comparing to that in BA or FA systems. Again, the influencing trend was  $\text{F}^- > \text{PO}_4^{3-} > \text{SO}_4^{2-}$ . However, in the case of phenol, the observed  $\text{H}_2\text{O}_2$  concentration was low, and the effect of anions on it was irregular, probably because its oxidation product benzoquinone can catalyze the degradation of  $\text{H}_2\text{O}_2$  [30]. On  $\text{TiO}_2$  with preadsorbed  $\text{F}^-$ ,  $\text{PO}_4^{3-}$  or  $\text{SO}_4^{2-}$ , similar results for  $\text{H}_2\text{O}_2$  concentration were observed: the anions decreased and increased the  $\text{H}_2\text{O}_2$  concentrations during the degradation of BA and FA systems, respectively (Fig. A.2).

Generally, the concentration of  $\text{H}_2\text{O}_2$  in  $\text{TiO}_2$  photocatalytic system is determined by both its formation (Eqs. (1–3), for example) and decomposition (Eq. (4) or (5)). Both the organic substrates and the anions can influence markedly these processes. For the

**Table 1**

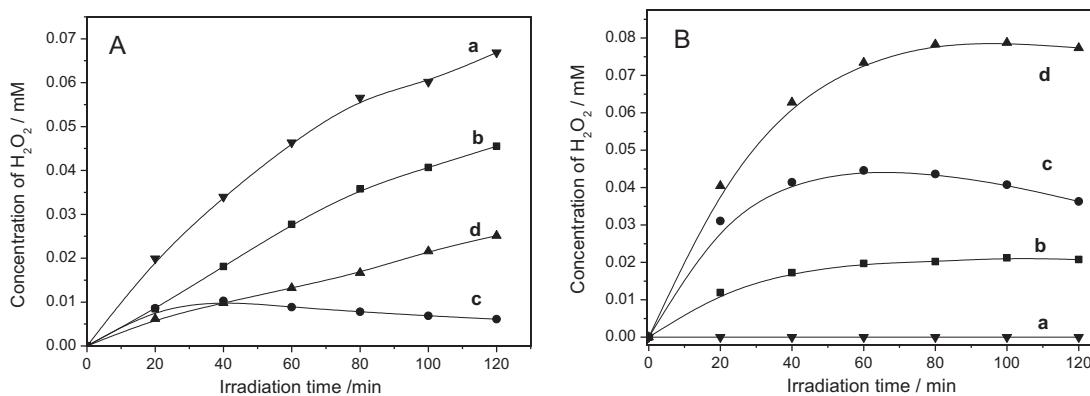
Apparent degradation kinetic of the different substrates in the presence of different anions (under photodegradation conditions in Fig. 1 and Fig. A.1).

		$\text{TiO}_2$	$\text{TiO}_2/\text{SO}_4^{2-}$	$\text{TiO}_2/\text{PO}_4^{3-}$	$\text{TiO}_2/\text{F}^-$
BA	Adsorption <sup>c</sup>	0.043	trace	trace	trace
	$k^a$	0.45	0.55	1.1	1.55
FA	Adsorption <sup>c</sup>	0.34	0.21	0.19	0.19
	$k^a$	1.22	0.88	0.46	0.54
Phenol	Adsorption <sup>c</sup>	trace	trace	trace	trace
	$k^b$	0.57	0.71	1.33	1.87
Benzene	Adsorption <sup>c</sup>	trace	trace	trace	trace
	$k^b$	1.07	1.25	1.61	2.38

<sup>a</sup> Fitted according to the zero-order kinetics, unit:  $10^3$  mmol/min.

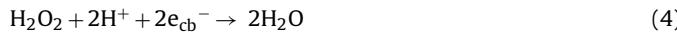
<sup>b</sup> Fitted according to the first-order kinetics, unit:  $10^2$  min $^{-1}$ .

<sup>c</sup> Unit: mmol/g.



**Fig. 2.** Hydrogen peroxide accumulation during photocatalytic degradation of (A) benzoic acid and (B) formic acid on naked TiO<sub>2</sub> (a) and in the presence of different anions (b: SO<sub>4</sub><sup>2-</sup>, c: PO<sub>4</sub><sup>3-</sup>, d: F<sup>-</sup>). Initial concentration of BA: 0.5 mM; FA: 2 mM; TiO<sub>2</sub>: 1 g/L; Concentration of anions: 2 mM; pH 3.5.

photocatalytic system of FA, as proposed by Mrowetz and Selli [7], the first one-electron oxidation of FA generates high reductive CO<sub>2</sub><sup>•-</sup> ( $E_0 = -1.9$  V vs. NHE). It can inject rapidly its electrons into conduction band on naked TiO<sub>2</sub> (current doubling effect, [31]). The surface fluorination can weaken the interaction of CO<sub>2</sub><sup>•-</sup> with TiO<sub>2</sub>, and accordingly eliminate largely the current doubling effect. CO<sub>2</sub><sup>•-</sup> is forced to react with dissolved O<sub>2</sub> to HO<sub>2</sub><sup>•-</sup> (Eq. (6)), and then to H<sub>2</sub>O<sub>2</sub>. This mechanistic proposal should also be applicable in PO<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup> cases, that is, the presence of anions on the surface not only inhibits the photocatalytic decomposition of formed H<sub>2</sub>O<sub>2</sub>, but also enhances the formation of H<sub>2</sub>O<sub>2</sub> in FA system. However, the explanation for the depressive effect of anions on the concentration of H<sub>2</sub>O<sub>2</sub> during benzoic acid (BA) degradation is not so well established. The surface adsorbed anions would block the generation of Ti—OOH, which is considered as the prior step for the decomposition of H<sub>2</sub>O<sub>2</sub> [9], and consequently hinder the decomposition of H<sub>2</sub>O<sub>2</sub>. Thus, the decreased H<sub>2</sub>O<sub>2</sub> concentration can be only attributed to its depressive formation. On the fluorination surface, Mrowetz and Selli argued that the lower H<sub>2</sub>O<sub>2</sub> evolution in the BA system was due to the decreased rate of the interfacial electron transfer in the presence of surface fluoride [7]. There are also other reasons that could be responsible for the lower H<sub>2</sub>O<sub>2</sub> evolution. For example, it is possible that the adsorption of anions changes the surface properties of TiO<sub>2</sub> and alters the pathway of the oxygen photoreduction to bypass the formation of H<sub>2</sub>O<sub>2</sub>. Further work is needed to address the detailed effects of anions on the oxygen reduction. Nevertheless, the most important to our point is that all the anions have similar influence on the formation, decomposition and consequently accumulation of H<sub>2</sub>O<sub>2</sub> during the photocatalytic degradation reactions of both BA and FA.

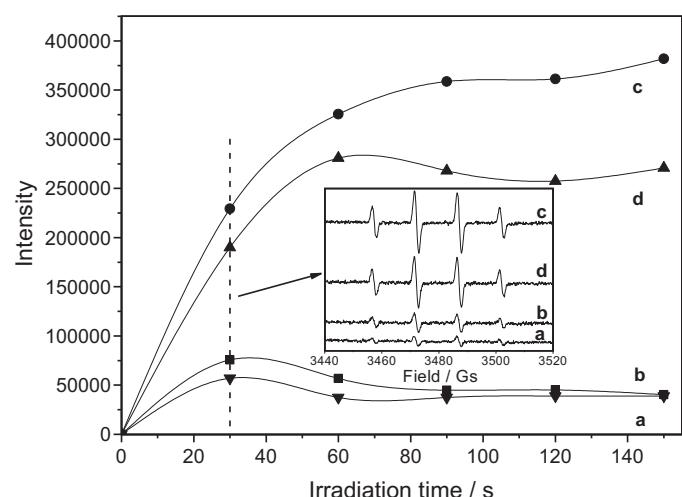


Based on the facts above, alternations on photocatalytic path occur after surface anionization of TiO<sub>2</sub>. To further investigate the mechanism of the alternations, we systematically examined the formation of •OH, a critical reactive species during photocatalysis, in the presence of different anions by spin-trapping EPR experiments. As shown in Fig. 3, F<sup>-</sup> and PO<sub>4</sub><sup>3-</sup> were also able to significantly enhance the generation of •OH. The signal intensity of DMPO-•OH adduct in the presence of 2 mM PO<sub>4</sub><sup>3-</sup> was ten times

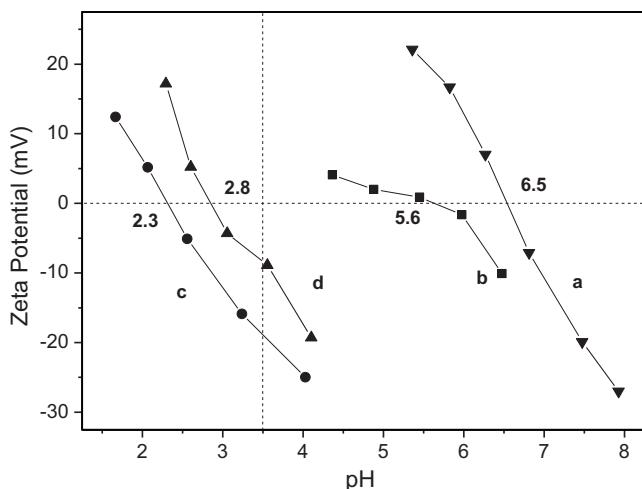
as high as that in naked TiO<sub>2</sub> suspensions. Addition of SO<sub>4</sub><sup>2-</sup> also increased slightly the formation of hydroxyl radicals especially at the beginning of irradiation.

Since •OH is the main active oxidization species in TiO<sub>2</sub> photocatalytic system, enhancement in free •OH radical means that, in the presence of anions, the free •OH radical may play more important role in degradation reaction than in naked TiO<sub>2</sub> suspensions [2]. On the other hand, the anions that specifically adsorbed on the surface Lewis acidic sites (Ti sites) will block competitively the interaction of the substrate and the formed intermediates with the surface (Table 1), and consequently the direct hole-transfer process between them will be hindered markedly. As a result, the substrates that are susceptible to •OH radical, such as BA, benzene and phenol, undergo more rapid oxidation in the presence of anions, while those with less •OH sensitivity such as FA and dichloroacetic acid [5] will exhibit less effective degradation. In our study, for example, the rate constant of the reaction between FA and •OH ( $k_{FA} = 1.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , [32]) is much less than that of BA ( $k_{BA} = 4.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , [33]). Accordingly, the anions speed up the oxidation of BA by enhancing the formation of •OH radicals, while slow down the reaction of FA by hindering the interaction between FA and TiO<sub>2</sub>.

Since the anions have common effects on various photocatalytic behaviors, the operative mechanism underlying these effects



**Fig. 3.** Intensity changes of EPR signal of the DMPO-•OH adduct generated in the TiO<sub>2</sub> dispersions with the irradiation time in the absence (a) or presence of different anions (b: SO<sub>4</sub><sup>2-</sup>, c: PO<sub>4</sub><sup>3-</sup>, d: F<sup>-</sup>). TiO<sub>2</sub>: 1 g/L; concentration of anions: 2 mM; DMPO: 40 mM; pH 3.5. Inset shows the EPR spectra after irradiation of 30 s.



**Fig. 4.** Zeta potentials of TiO<sub>2</sub> particles (50 mg/L) in aqueous suspensions as a function of pH in the absence (a) or presence of 2 mM anions (b. SO<sub>4</sub><sup>2-</sup>, c. PO<sub>4</sub><sup>3-</sup>, d. F<sup>-</sup>). pH was adjusted by HClO<sub>4</sub>.

should be relative to the unique characteristics of anions. We notice that anions with high specific-adsorption ability such as F<sup>-</sup> and PO<sub>4</sub><sup>3-</sup> have more significant effects than the less- or non-specifically-adsorbed ones (SO<sub>4</sub><sup>2-</sup> and ClO<sub>4</sub><sup>-</sup>). It was reported that the specifically-adsorbed anions can make the surface negatively charged [14,34]. These facts make us hypothesize that the surface charge may be essential to anionization effect. To verify this hypothesis, the effect of anions on surface charge was compared by measuring electrophoretic mobility of the particles. Fig. 4 showed the variation of zeta potentials of suspended TiO<sub>2</sub> particles in water as a function of pH in the presence of anions. The measured point of zero zeta potential (PZP) of naked TiO<sub>2</sub> was about pH 6.5, which was in agreement with the literature value [5]. The PZP changed to pH 2.3, 2.8, and 5.6, in the presence of PO<sub>4</sub><sup>3-</sup>, F<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, respectively. At the pH (3.5) and the anion concentrations (2 mM) employed in above degradation experiments, the surface of the photocatalyst in F<sup>-</sup> or PO<sub>4</sub><sup>3-</sup> systems is strongly negative-charged, due to the replacement of surface-adsorbed H<sub>2</sub>O by the anionic F<sup>-</sup> or PO<sub>4</sub><sup>3-</sup> species. By contrast, the particle surface bears positive charges in naked and SO<sub>4</sub><sup>2-</sup>-added systems. An extrapolation of the zeta potential curves indicates that the surface should have much less positive charge in the presence of SO<sub>4</sub><sup>2-</sup> than that of the naked TiO<sub>2</sub> at pH 3.5. The specific change of PZP for each anion on the naked TiO<sub>2</sub> is corresponded to its adsorption isotherm (Fig. A.4). The fitted Langmuir–Hinshelwood adsorption constant on TiO<sub>2</sub> is  $6.91 \times 10^{-3}$ ,  $5.61 \times 10^{-3}$  and  $1.81 \times 10^{-3} \text{ M}^{-1}$  for F<sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, and SO<sub>4</sub><sup>2-</sup>, respectively, and the maximum adsorption amount is 0.366, 0.226, and 0.118 mmol/g, respectively. Considering the possible chelating structure and the multi-charges of phosphate ion, the shift of PZP by PO<sub>4</sub><sup>3-</sup> is comparable to that by F<sup>-</sup> regardless of the lower adsorption capability comparing to the former. For SO<sub>4</sub><sup>2-</sup>, the relative less adsorption capability may be responsible for its weaker anionization effect comparing to F<sup>-</sup> and PO<sub>4</sub><sup>3-</sup>.

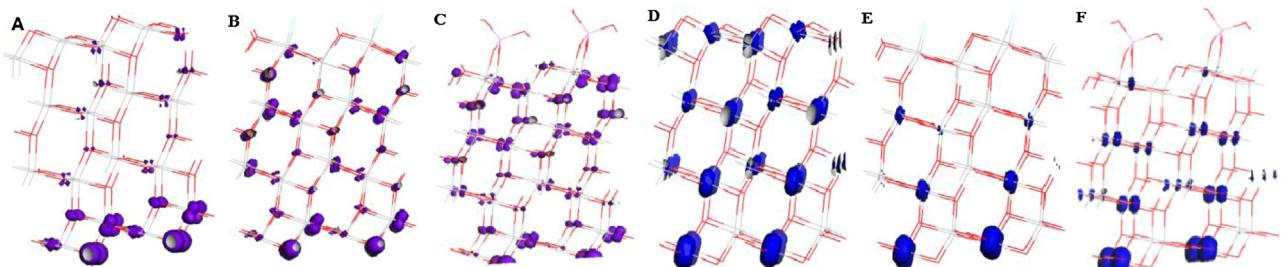
The good correlation of their effects on photocatalytic behaviors with the surface charge confirms the important role of surface charge on photocatalytic properties. To make clear the effect of the anions on the charge separation and surface electron transfer process, the effect of anions on the energy band structure and the distribution of the electrons and holes were investigated by periodic density functional theory (DFT). The gradient corrected DFT is known to markedly favor the electron delocalization due to its inherent self-interaction error [35–37]. It may give a delocalized character for the localized excess charges and lead to significant

underestimation of the band gap. Nevertheless, a qualitative comparison between different surfaces at the same theory level will be informative for our understanding of charge separation, because we are more interested in a comparison than in the absolute values of density of states and carrier distributions.

As proven by the zeta potential experiments, the anionized surface is negatively charged at the pH employed in this study, whereas it is positive in naked TiO<sub>2</sub>. Accordingly, the calculation was performed on the surface with negative or positive charges for these two cases, respectively, by removing or attaching a proton from or onto the electroneutral surface. Fig. A.5 (A–C for the neutral surfaces and D–F for the charged ones) shows the density of state (DOS) of different surfaces and the projected DOS on surface adsorbed species. The following observations can be made: (1) Effect of all the examined species on the band gap of the photocatalyst is quite limited, and all the adsorbents do not present any additional electronic states inside the band gap of the semiconductor. It means that the adsorption of the anions and the presence of surface charge are unable to change the absorption edge of the photocatalyst, which is consistent with the reported experiments that insignificant spectra change was observed upon the adsorption of the anion [5,38]. (2) Water adsorbs on (101) anatase surface in a molecular mode, and its dissociative adsorption is not favored, which is in line with the earlier theoretical and experimental results [39,40]. More importantly, the electronic states that originate from the adsorbed water are located inside deep valence band, which suggests that it is difficult for H<sub>2</sub>O molecule to be adsorbed on Ti sites to be oxidized by holes. This can interpret the observation of low •OH radical concentration in the naked TiO<sub>2</sub> system (Fig. 3). (3) HF and H<sub>3</sub>PO<sub>4</sub> prefer to adsorb dissociatively on the (101) surface. The states derived from HF in both its neutral and anionic forms are embedded deeply in the valence band, indicating that the F species cannot be oxidized by VB holes. For the H<sub>3</sub>PO<sub>4</sub> modified surface, although the states from the neutral H<sub>3</sub>PO<sub>4</sub> are in the deep VB, some electronic states from the adsorbed H<sub>2</sub>PO<sub>4</sub><sup>-</sup> anion are rather shallow relative to the bottom of VB.

As electron-transfer processes at the semiconductor/electrolyte interface are strongly affected by the density of available carriers (electrons and holes) at the semiconductor surface. It will be helpful to inspect the effect of the adsorbed species on the state density of the surface atoms. It is known that the valence and conduction band of TiO<sub>2</sub> are mainly derived from the 2p orbitals of the oxygen and 3d orbitals of Ti atoms, respectively. Accordingly, we projected the density of states on the O and Ti atoms on the first layer of the slab to demonstrate the surface availability of the holes and electrons, respectively (Fig. A.6 in Supplementary Data). For the surfaces with adsorbed fluoride and phosphate species, the effects of neutral HF and H<sub>3</sub>PO<sub>4</sub> on the PDOS of surface oxygen are very insignificant near the band edge, while the negative charged surface exhibits PDOS above VB top of the naked TiO<sub>2</sub> (Fig. A.6B and C). These results imply that the surface oxygen can trap more photogenerated holes when the anions adsorb on the surface. Although the adsorption of neutral H<sub>2</sub>O can exhibit the similar function to enhance the hole-trapping on surface according to our calculation (Fig. A.6A), it is not applicable to our experiments, in which the surface is positively charged by protonation (Fig. 4). For the protonated surface with adsorbed H<sub>2</sub>O, the surface oxygen has similar PDOS near the VB top to that of the naked TiO<sub>2</sub> (Fig. A.6A).

For the distribution of the conduction band electron, naked TiO<sub>2</sub> and protonated surface with H<sub>2</sub>O show similar PDOS on the surface Ti atoms, while the surface with neutral H<sub>2</sub>O, HF, or H<sub>3</sub>PO<sub>4</sub> has PDOS shifted into CB, and the adsorption of F<sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> anions moves the PDOS further into deep CB, suggesting that fewer CB electrons are expected on the surface with the adsorbed fluoride and phosphate species in both their neutral and negative forms. This result indicates that, rather than to be trapped at the surface



**Fig. 5.** Valence band hole (A–C) and conduction band electron (D–F) distributions in the surface slab with different charged adsorbents modeled by adding or removing of a single electron into or from the supercell. (A) and (D): naked  $\text{TiO}_2$ ; (B) and (E): with adsorbed HF but one proton lost; (C) and (F): with adsorbed  $\text{H}_3\text{PO}_4$  but one proton lost.

$\equiv\text{Ti}-\text{F}$  groups as proposed by Park and Choi [5], the photogenerated electron tends to move away from surface after  $\text{F}^-$  and other anions are adsorbed on the Ti sites by replacing water molecules.

The distribution of conduction band electrons and valence band holes in the photocatalyst was further modeled by adding or removing a single electron into or from the super cell. Spin densities for the charge surfaces are shown in Fig. 5. In well agreement with the results on density of states, in the negative charged surfaces with adsorbed  $\text{F}^-$  and  $\text{H}_2\text{PO}_4^-$  anions, VB holes are markedly attracted toward the surface of  $\text{TiO}_2$  (Fig. 5A–C). These results confirm that, at the negative charged surface, the hole would be easier to be trapped on the surface. However, as shown in Fig. 5D–F, on the negative surface, the electron would be pushed deeper into the inner Ti atoms.

In the classical semiconductor photoelectrochemistry, the photoinduced charge transport and separation is attributed to the electric field formed in the space charge layer (band bending) which is induced by the charge in the Helmholtz double layer in the electrolyte side of interface. Although it is still questionable for the occurrence of the band bending in the nanocrystalline semiconductor, it is apparent that the covering of the catalyst surface with negatively charged anions could form an electrostatic field in the surface layer of  $\text{TiO}_2$ . The direction of the electric field is from the bulk to the surface of  $\text{TiO}_2$  such that any excess holes created in the space-charge region would move toward the surface while any excess electrons would move toward the bulk semiconductor. As the surface recombination between the electrons and holes is one of the most important recombination routes during photocatalysis, the different moving direction of electrons and holes in presence of anions can markedly enhance their separation and consequently suppress charge recombination. Under ultraviolet irradiation, an electron in the valence band in  $\text{TiO}_2$  is excited to the conduction band to leave a positive hole in the valence band. The hole is drawn to the  $\text{TiO}_2$  surface by the electrostatic force, and thus its reaction with the surface adsorbed reductive species is facilitated. In well agreement with our theoretical results, Jing et al. [41] observed experimentally that photogenerated holes in the phosphate-modified  $\text{TiO}_2$  film exhibited a slightly faster decay dynamic than the electrons, while the holes and the electrons underwent the same dynamic in the unmodified film. They also found that the photogenerated charges of the phosphate-modified  $\text{TiO}_2$  had a much longer lifetime than those of the unmodified one, and the modified electrode exhibited higher photoelectrochemical efficiency for water oxidation.

The question is why the water oxidation to hydroxyl radical by the hole is enhanced upon the addition of anions, while the hole directly transfer to FA and BA is hindered under the same conditions. It is known that, in aqueous solution,  $\text{H}_2\text{O}$  and FA prefer to adsorb molecularly and dissociatively on the surface Ti atoms, respectively. In these interactions,  $\text{H}_2\text{O}$  and FA act as Lewis base, while the Ti atoms act as acid. Because the Lewis basicity of the dissociative FA is much higher than the molecular  $\text{H}_2\text{O}$ , the

adsorption of FA is much stronger than  $\text{H}_2\text{O}$ . In addition, FA is easier to be oxidized than the  $\text{H}_2\text{O}$ . As a result, in aqueous solution, FA traps the hole prior to  $\text{H}_2\text{O}$ . On the other hand, in the presence of anions, the surface Ti atoms are occupied by the specific adsorbed  $\text{F}^-$  and  $\text{PO}_4^{3-}$  (stronger Lewis bases than formate), and the Lewis acid–base interaction between  $\text{H}_2\text{O}/\text{FA}$  and Ti is blocked by the anions. Still,  $\text{H}_2\text{O}$  can interact with the surface bridging oxygen, the adsorbed  $\text{F}^-$  or the oxygen in phosphate through hydrogen bond. However, the interaction between these hydrogen-bond acceptors and FA is believed to be quite weak because of the strong acidity of FA ( $\text{pK}_a = 3.44$ ). Moreover, the concentration of solvent  $\text{H}_2\text{O}$  is much higher than that of FA. This is able to well interpret our experimental observation that the formation of hydroxyl radical is enhanced, whereas the degradation of FA is suppressed after the addition of anions. It is worth noting that the effects of anionization on the photocatalytic processes are diverse aspects and also complicated. For example, besides the effect on the charge separation, the adsorption mode and equilibrium of the substrates at the water– $\text{TiO}_2$  interface, the surface anionization is also expected to greatly influence the reductive half reaction of photocatalysis (the reaction between the  $\text{O}_2$  and conduction band electron), as suggested by the formation of reaction intermediate  $\text{H}_2\text{O}_2$ . All these would be substrate-dependent and change the overall photocatalytic behavior.

#### 4. Conclusions

In the present study, we provide our experimental and theoretical evidences that the specific-adsorbed anions such as  $\text{F}^-$ ,  $\text{PO}_4^{3-}$ , and  $\text{SO}_4^{2-}$  are able to cause similar effects on the photocatalytic process. These effects originate from a common mechanism that is based on the anion-derived surface negative charges, which draw the photogenerated holes to the  $\text{TiO}_2$  surface by the electrostatic force and consequently enhance the oxidation of the surface adsorbed species. As a result,  $\cdot\text{OH}$ -sensitive organic pollutants such as benzoic acid, benzene and phenol can undergo as more rapid degradation, while degradation for those less  $\cdot\text{OH}$ -susceptibility such as formic acid will be hindered due to their weakened adsorption on the surface. Such a common mechanism may have many implications on the application of photocatalysis for the degradation of organic pollutants. First, it provides a potential strategy to improve the photocatalytic performance by surface anionization. Second, our study suggests that the anions existing in the photocatalytic systems, especially those with specific-adsorption ability, should be in no way overlooked, when one evaluates the photocatalytic performance or seeks the photocatalytic mechanism. In addition, most of the proposed strategies to improve the photocatalytic activity so far, for example, loading noble metals Pt, Pd, and Ag on the oxide surface, are based on the enhancement of the reactivity of  $e_{cb}^-$ , less attention has been paid to promote the kinetics of the interfacial abstraction of the holes. The anion effect highlighted in this study may represent a good example to

manipulate the photocatalytic performance by the tuning the hole availability.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2013.03.001>.

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